(54) IMPROVEMENTS IN POLYALKYLENE FILAMENTS, STAPLE FIBRE AND YARNS

(71) We, FIBER INDUSTRIES, INC., of Post Office Box 10038, Charlotte, North Carolina, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to resilient polyalkylene terephthalate filaments and to fibrefill and pile face yarns produced therefrom.

Polyesters derived from terephthalic acid or its derivatives are known to possess sufficient resilience in filament form to warrant commercial use of the filaments in areas of the textile industry where resilience is a major product requirement, e.g. carpets, pile fabrics and fibrefill. The polyester filaments which have found wide acceptance by the textile industry are made from polyethylene terephthalate. However, the physical properties of such filaments are not as good as could be desired for carpet pile or fibrefill of the highest quality especially as regards resiliency which, in terms of bending recovery, as hereinafter defined, ranges from 45% to 55%.

In the description and claims filament resilience is defined in terms of "bending recovery" the value of which is determined at 20% surface strain, with filaments having a circular cross section, as follows:—ten turns (n_1) of the filament are wound on to a wire of known diameter under a wrapping tension of 0.04 grams per denier at a rate of 20 turns per minute. After 30 seconds the filament is cut just beyond the last turn and, after a recovery period of one minute, the number of turns (n_2) remaining is counted. The bending recovery is given by

[Price 25p]

$$(1 - 0.1 \times n_2) \times 100\%$$

The surface strain (e) of the bent filament can be varied by using wires of different diameter (D) and is computed as a percentage, from the formula

$$e = \left(\frac{d}{D+d} \right) \times 100$$

where d is the filament diameter.

When bending recovery of a crimped filament is to be determined, the filament is first subjected to a temperature of 175°C. under a tension of .05 grams per denier for a period of 5 minutes. The bending recovery tests are then made according to the procedure described above.

The present invention comprises crimped polyester filaments and staple fibre having a bending recovery of at least 65%, more than 6.0 crimps per crimped inch and more than 18% crimp and made from polyester whereof 50% or more by weight is a polymeric terephthalic acid ester of 1,4-butane-diol or 1,3-propanediol. The invention provides filaments and fibre which exhibit superior performance as pile in pile fabrics or as fibrefill compared with products made from polyethylene terephthalate.

In the description and claims the number of crimps per crimped inch of a filament is assessed by taking the average of the number of crimps in 20 one-inch lengths of filament held straight under insufficient tension to open the crimps while the percentage of crimp is determined by taking a known length L_c (under zero tension) of filament and measuring its length L_u under just enough tension to remove all the crimp from the filament. The

percentage crimp is then calculated from the formula

$$\% \; Crimp = \frac{L_u - L_c}{L_u} \times 100$$

In addition to the properties used in defining the filaments and fibres of the invention, the initial tensile modulus, tensile recovery, tensile work recovery of the uncrimped filaments from which the crimped filaments and staple fibre of the invention are made are important in determining the usefulness of the crimped products as pile yarn or fibrefill as is the relative viscosity of the polymer used.

The "initial tensile modulus" (represented by the symbol Mi) is defined as the slope of the first reasonably straight portion of a stress-strain curve of the funicular structure obtained by plotting tension on a vertical axis vs. elongation on a horizontal axis as the structure is being elongated at the rate of 10% per minute under standard conditions of temperature (21° C.) and humidity (60% RH). In almost every instance, this first reasonably straight portion is also the steepest slope to be found on the curve. The values as used herein are in units of kilograms per square millimeter per 100% elongati n. A low-tensile modulus is indicative of a preferred filament.

The "tensile recovery" (TR) is defined as the extent to which a filament recovers its original length after being stretched, a stress-strain curve being used to determine tensile recovery under the testing conditions. The test consists in extending the funicular structure at a constant rate of elongation of 10% per minute. A specimen is held at the maximum elongation desired for 30 seconds, e.g., by the use of a time switch, and is then allowed to retract at the same rate at which it was extended. The specimen is extended 5.0% for each determination. The extensi n during elongation and the recovery during retraction are measured along the elongation axis. The percent tensile recovery (TR_s) is then the ratio of the extent to which the filament retracts to the extent to which it was elongated times 100. This test is run under standard conditions at 60% RH and 21° C. When a stress-strain curve is plotted from tensile recovery, values for "work recovery" may be obtained from the equation

$$work \; recovery = \frac{area \; under \; recovery \; curve}{area \; under \; extension \; curve} \times 100$$

The relative viscosity (R.V.) of a polymer in this specification is the ratio of the viscosity of a solution of 8 grams of the polymer in 100 millilitres of freshly distilled orthochlorophenol, at a temperature of 100° C. and after being kept at that temperature for approximately 30 minutes to the viscosity of freshly distilled orthochlorophenol measured in the same units at 25° C.

The invention is especially concerned with filaments, yarns and staple fibre having a bending recovery of at least 90%, an initial tensile modulus of less than 350 kg/mm², a tensile recovery (TR_s) of greater than 60% and a work recovery (WR_s) of greater than 30% and made from a polyester of the kind referred to having a relative viscosity greater than 12 and, in the case of polytetramethylene terephthalate, greater than 18.

Yarns made from continuous filaments or staple fibre according to the invention can be employed in making woven, knitted or non-woven fabrics and as the pile of pile fabrics, including carpets, while both tows of continuous filaments and loose staple fibre are useful as fibrefill, i.e. stuffing material for such articles as pillows.

Crimping methods which may be employed in conjunction with this invention are stuffer box crimping, steam jet or other hot fluid crimping and gear crimping. The preferred method for crimping filaments to be cut into staple fibre is by means of a stuffer box crimper, the filaments, without pretreatment, being partly stress relaxed in the crimper stuffer box by injection of steam or other hot fluids and preferably being crimped, especially in the case of carpet stample fibre, so as to produce at least 9.0 crimps per crimped inch and at least 20.0 percent crimp.

The filament-forming material may consist wholly of polytrimethylene terephthalate or polytetramethylene terephthalate or it may be a blend of a copolymer. The preferred polymer is polytetramethylene terephthalate or a blend of this polyester with up to an equal weight of another polyester; polytrimethylene terephthalate will not tolerate blending with as much of another polyester for the production of filaments having a blending recovery of at least 65%. Examples of suitable glycols for use in making copolymers or polymers for blending are hydroquinone; cis and trans- cyclohexanedimethanol; 1,1 - bis-(hydroxymethyl) - cyclohexane; 2,2,3,3-tetramethyl - 1,3 - cyclobutanediol; 1,4-cyclohexanediol; ethylene glycol; 1,5-pentanediol; 1,12-dodecanediol; diethylene glycol; triethylene glycol; 2,2-dimethylpropanediol-1,2; 2,2,3,3,4,4 - hexafluoropentanediol-1,5; decahydro - 1,2 - bis - (hydroxymethyl)-naphthalene; 4,4' - dihydroxybiphenyl; 4,4'-dimethanolhexahydrobiphenyl; bis - (4-hydroxyphenyl) methane; bis - (4 - hydroxy-

phenyl) ether; bis - (4 - hydroxyphenol) sulfone; bis - (4 - hydroxyphenyl) ketone; bis - (4 - hydroxyphenyl) sulfoxide; 2,2-bis(4-hydroxyphenyl)hexafluoropropane; 2,2-bis - (4 - hydroxyphenyl) propane; bis(4-hydroxyphenyl) cycl hexylmethane; 2,5-norbornanediol; phenolphthalein; bis-(4-hydroxyphenyl) oxindole; 1,4 - bicyclo(2.2.2) octanedimethanol; 9,10 - bis(β - hydroxyethyl) octahydroanthracene; trimethylol ethane; pentaerythritol; methyl diethanolamine; t-butyl diethanolamine; dechaydro-1,5-bis-(hydroxymethyl) naphthalene; decahydro-1,8-bis(hydroxymethyl) naphthalate; decahydro-2,3-bis(hydroxymethyl)naphthalene.

Examples of suitable dicarboxylic acids which can be used in copolymers with or in polymers for blending with poly(1,3-propylene terephthalate) and poly(1,4-butylene tere-phthalate) are isophthalic acid; hexahydro terephthalic acid; homophthalic acid; para-carboxyphenoxyacetic acid; para-carboxy-phenylacetic acid; 8-(para-carboxyphenyl)-octanoic acid; phenylenediacetic acid; chloro-terephthalic acid; fluoroterephthalic acid; 2,5-di-chloroterephthalic acid; 4-chloroisophthalic acid; 3,6-bis(carboxymethyl)durene; oxalic acid; adipic acid; sebacic acid; 1,4-naphtha-lenedicarboxylic acid; 1,5-naphthalene-dicar-boxylic acid; 2,6-naphthalenedicarboxylic acid; 2,7-naphthalenedicarboxylic acid; 4,4'-dicarboxybiphenyl; 3,3' - dicarboxybiphenyl; bis - (4 - carboxyphenyl) butane; bis - (4-carboxyphenyl) octane; bis - (4 - carboxy-phenoxy) ethane bis - (4 - carboxyphenoxy) hexane; bis - (4 - carboxyphenylmethyl)-ether; bis - (4 - carboxylphenylmethyl) ketene; biphenylenediacetic acid; biphenylene-dibutyric acid; bis - (4 - carboxyphenyl) ether; (bis - (4 - carboxyphenyl) sulfide; bis-(4 - carboxyphenyl) sulfone; bis - (4 - car-boxyphenyl)ketone; 4,4' - dicarboxybenzani-lide; bis - (4 - carboxyphenoxyethane); bis-(4 - carboxy - thiophenoxy) ethane; ethyl bis - (4 - carboxyphenyl) amine; 2, - 8 - di-benzofurandicarboxylic acid; 1,4 - bicycio (2.2.2) octane dicarboxylic acid; cis and trans 4,4'-stilbenedicarboxylic acid.

Hydroxy acids may also be usually em-ployed, for example: 4-hydroxybenzoic acid; 3 - chloro - 5 - hydroxybenzoic acid; 4-(2 - hydroxyethyl)benzoic acid; poly(ethyl-ene diphenoxyethane - 4,4' - dicarboxylate) p - (ω - hydroxyalkylbenzoic acid); aliphatic hydroxy acids or their lactones such as propio--lactone and γ-hydrobutyric acid.

The polytetramethylene terephthalate poly-mer may be prepared by either ester inter-change processes or by direct esterification processes. Examples of the former processes are given in British Patent No. 578,079, while examples of the latter process are given in British Patent No. 777,628. Similarly, poly-trimethylene terephthalate polymer may be prepared by replacement of the 1,4 butane-diol by 1,3 propanediol in the previously men-ti ned processes. Additional information on poly(methylene terephthalate)processes and the properties of the uncrimped products may be had from *Journal of Polymer Science*: Part A—1, Vol. 4, 1851—1859 (1966).

The following Examples I, II and IV to IX illustrate the invention; Example III is given for purposes of comparison and does not embody the invention.

EXAMPLE I

Fifteen pounds of dimethyl terephthalate, 8.9 pounds of tetramethylene glycol, 0.0013 pounds of sodium and one pound of mag-nesium ribbon are heated together at 197° C. in a reaction vessel subjected to a stream of oxygen-free nitrogen for one and one-quarter hours. The resulting low polymeric tetramethylene terephthalate is then heated at 280° C. for 30 minutes under atmospheric pressure and for a further period of three hours under a slight vacuum. The resulting polymer having an R.V. of 25.3 is then re-duced to chip form and the chip dried to a moisture level of less than 0.015%.

The chip is formulated into a melt and ex-truded through an annular pack containing 96 holes each having a diameter of 0.018", the extrusion being conducted at a rate of 34.3 lbs. per hour, maintaining a pack outlet tem-perature of about 260° C. The extrudate is subjected to an outflow quench at a flow rate of 80 cubic feet per minute, and the re-sultant filament bundle taken up at a wind-up speed of 2000 feet per minute resulting in a spun denier per filament of 40. A spin finish is then applied, the spin finish compris-ing a non-ionic and cationic lubricating agent, together with an anti-static agent, all of which are in aqueous solution. The pick-up is ad-justed so that the finish level on the filament bundle is approximately 0.05% by weight.

The filaments as spun have a bi-refringence in the range from 0.070 to 0.080; the filament bundle drawn through a hot water immer-sion bath at 82° C. to effect a draw ratio f 3.20 to 1 and the drawn product is then passed through a finish bath comprising a nonionic lubricant and a cationic lubricant, and an anti-static agent, all of which are in an aqueous medium. The finish level is ad-justed so as to produce a pick-up of 0.30% by weight on the filament bundle which is then passed into a stuffer box crimper and a crimp level of 11 crimps per inch is ob-tained. The crimped product is then heat set into tow form by subjecting it to tempera-tures of about 150° C. for a period of 18 minutes, after which the heat set tow is cut into 6" staple lengths. The resultant staple fibre is found to have a tenacity of 3 to 3.6 grams per denier and an elongation to break of 50 to 60 percent. Bending recovery is found to be 85%.

EXAMPLE II

The process of Example I is repeated with the exception that the polymer chip is produced as follows: 830 parts terephthalic acid (5 mol), 1125 parts 1,4 butanediol (12.5 mol) and 0.04 parts sodium hydroxide are reacted over the range of 230—260° C. in a stirred autoclave. The pressure is maintained at 50—60 psig throughout. The water formed in the reaction together with any by-product tetrahydrofuran is periodically bled off. After about one hour the rate of pressure build-up is found to fall off and eventually ceases. Pressure is then let down to 1 atmosphere, 0.25 antimony trifluoride added and the remaining ester polycondensed at 260° C. and 0.2 mm. pressure over a period of 135 minutes. Polytetramethylene terephthalate having an R.V. of 25.4 is obtained and is reduced to chip form.

The chip is then spun, drawn, crimped and cut into staple lengths, according to the process as outlined in Example I. The staple fibre is found to have a tenacity of 3 to 3.6 grams per denier and an elongation to break of 50 to 60 percent. Bending recovery is 83%.

EXAMPLE III

830 parts terephthalic acid (5 mol) and 775 parts ethylene glycol (12.5 mol) are reacted at 200—250° C. in a stirred autoclave fitted with a short fractionating column, condenser and receiver suitable for operation under pressure. The system is vented to atmosphere during the initial heating to 200° C. and pressure is then increased to 55 psig with oxygen-free nitrogen. As esterification proceeds, water is distilled from the column top at a temperature of 150—155° C., pressure being maintained at 55 psig throughout. The reaction is found to be complete in 150 minutes and is then followed by a polycondensation reaction which is found to be complete in 120 minutes. The final polyester is found to have an R.V. of 14.7; softening point 258° C. and color 1.8. The polymer is then reduced to chip form and the chip dried to a moisture level of less than 0.015 percent by weight.

The chip is formulated into a melt and extruded through an annular pack containing 96 holes of 0.024" diameter at a rate of 45.6 pounds per hour, the pack being maintained at an outlet temperature of 278° C. The extrudate is subjected to an outflow quench at a flow rate of 80 cubic feet per minute and is wound up at a speed of 2000 feet per minute so that a spun denier per filament of 53.4 is obtained. A spin finish is then applied to the filament bundle, the spin finish comprising non-ionic and cationic lubricating agents together with anti-static agents in a water solution. The bath is adjusted so as to produce a pick-up of 0.07 percent by weight on the tow. The filaments as spun are found to have a birefringence in the range of 0.0014 to 0.0024 and to be completely amorphous. The filament bundle is then subjected to the drawing, crimping and staple forming operations as set forth in Example I. The staple fibre is found to have a tenacity of 3.0 to 3.6 grams per denier and an elongation to break of 50 to 60 percent. Bending recovery is found to be 48%.

In order to evaluate the suitability of the staple fibre in carpet face yarns, yarns are formulated from the polytetramethylene terephthalate products of Examples I and II, and compared with similar yarns formulated from the polyethylene terephthalate staple fibres of Example III. 16 denier per filament staple fibre is employed to prepare yarns having a 2.0/2 cotton count, the singles having 3.5 turns of Z twist, and a ply twist of 3 turns per inch S twist. These yarns are then used in making cut pile carpets, having a pile weight of 35 ounces per square yard and a pile height of 9/16 inch, by tufting 6.5 stitches per inch with a 5/32 gauge tufting machine into a 36" wide jute backing. Sample specimens measuring 36" × 18" with the 18" width direction parallel to the warp are then prepared. Test samples are vacuumed and allowed to relax freely for 24 hours. The original pile thickness is then determined at 0.75 psig. The tested samples are then placed in a traffic pattern wherein traffic is measured by a 100,000 step counter (manufactured by Vedder-Root, Hartford, Connecticut, United States of America). After 5000 steps had been counted, the samples are removed and a thickness measurement is taken. The samples are then vacuumed and replaced in testing. Measurements are repeated for 10,000 steps and 20,000 steps. Samples are then shampooed, vacuumed, allowed to relax for two hours, and again measured for thickness. The samples are then once more subjected to the traffic pattern, and removed after a total of 30,000 and 50,000 steps. Percent thickness retained (at each step level) is then determined as compressed thickness over original thickness multipled by 100. As a result f this testing procedure, the following values are obtained, as reported in the following table designated as Table I:

TABLE I
Step Level — Percent Thickness Retained

	Example I	Example II	Example III
0	100.0	100	100
3,500	96.3	95.8	92.0
8,500	93.8	93.5	85.9
21,000	89.0	88.5	77.6
After Shampoo	98.5	98.0	84.6
32,400	86.1	86.0	71.0
46,100	83.0	83.5	67.7

EXAMPLE IV

800 grams of dimethyl terephthalate, 665 grams of trimethylene glycol and 15 ccs. of NaH[Ti(OBu)₆] are heated together at 230° C. in a reaction vessel subjected to a stream of oxygen-free nitrogen for 210 minutes; the resulting low polymeric trimethylene terephthalate is then heated at 250° C. for 210 minutes, at a pressure of 0.4 mm mercury. The resulting polymer is found to have a relative viscosity of 18.0, a carboxyl end group value of 14.8 and a melting point of differential thermal analysis of 222.0° C.

The chip is then formulated into a melt, spun, drawn and crimped according to the process as outlined in Example I. The continuous filaments are found to have an initial tensile modulus of less than 350 Kg/mm² a tensile recovery (TR₁) of greater than 60% and work recovery (WR₁) of greater than 30% and a bending recovery of from 70% to 100%.

EXAMPLE V

800 grams of dimethyl terephthalate, 665 grams of trimethylene glycol and an ester interchange catalyst made up of 0.28 grams Tyzor "TBT", a catalyst manufactured by E. I. du Pont de Nemours, ("Tyzor" is a Registered Trade Mark) and 0.28 grams of MgCO₃ are heated together at 240° C. for a period of 356 minutes; the resulting low polymeric trimethylene terephthalate is then heated for 235 minutes at a temperature of 250° C. in the presence of 0.48 grams of macerated antimonic acid polymerization catalyst. The resulting polymer is found to have a relative viscosity of 18.6, a carboxyl end group value of 5.3, and a melting point determined by differential thermal analysis of 219.5° C. After the polymer is reduced to chip, the chip is spun and drawn, crimped and cut into staple length according to the process as outlined in Example I. The staple length fibres are found to have a satisfactory bending recovery.

EXAMPLE VI

Polymer prepared according to the procedure set forth in Example I is extruded through a spinnerette so as to produce 2.25 denier tow, the tow is then converted to 3″ staple fibre on a tow-converting device. Staple fibre is then spun to a 7.75 turn per inch, 10/1 cotton count yarn. The yarn is then knit on a 30″ 22-gauge Tompkins spring needle machine to produce a fabric having a 14.5 ounce per square yard weight and having all polytetramethylene terephthalate face yarns on a cotton backing. The resultant knit fabric is then napped as follows: Two low energy passes are made through a napper, followed by one low energy pass made through a double action napper. The back of the fabric is then coated with latex resin and cured at 325° F. for two minutes. A final low-energy pass is made through a single action napper to comb the fabric.

Two additional knit fabrics, identical in all respects, with the exception that, in one case, the staple fiber was polyethylene terephthalate polymer while, in the second, polytrimethylene terephthalate polymer prepared according to the process of Example IV is employed in preparing the staple fiber. The three fabrics are laundered at 120° F. and dried. Subsequent wear trials are found to show that the polytetramethylene terephthalate fabric and the polytrimethylene terephthalate fabric have superior resilience retention compared with the polyethylene terephthalate pile fabric.

EXAMPLE VII

Polymer prepared according to the process set forth in Example I is extruded through a spinnerette to produce 5 denier per filament tow. The final tow product is then subjected to a stuffer box crimping operation to produce 10 crimps per inch and then cut into 2½″ fibres. The fibres are then processed in a garnet machine and converted to

10 oz. batting. The batting is cut to 10″ × 10″ size and stacked in units of 3. The three unit test specimen is then placed in a Rubber Manufacturers Association tester which has as its principal parts a 50 square inch presser foot, a 250 pound capacity scale, a scale dial for determining distance of presser foot from the table loading top at any load, and a movable table top with a speed control device. The sample is inserted between the presser foot and the table top and the table top raised until a one pound load is indicated. The height of the specimen is then measured and recorded as initial loft. The table is again raised for a plurality of load increments until the 50 pound load is reached. Each of these increments is measured as compressed loft. In order to determine loft retention, a similar sample consisting of three stacked 10″×10″ squares of batting is placed in the corner of an ordinary muslin pillow casing. A 170 lb. weight is then repeatedly lowered on the sample at a rate of 60 cycles per minute, the weight being selected and designed so as to simulate a load received by a furniture cushion. At the end of 5000 cycles, the sample is placed in the Rubber Manufacturers Association test machine, and the percent loss of loft is determined at various loads. When the polytetramethylene terephthalate batting is compared with a polyethylene terephthalate batting which is similar in all respects with the exception of the polymer employed, and with a polytrimethylene terephthalate batting

which is also similar in all respects with the exception that the polymer employed is prepared according to the process set forth in Example IV, it is found that the polytetramethylene terephthalate batting and the polytrimethylene terephthalate batting have significantly lower losses in loft than the polyethylene terephthalate batting.

EXAMPLE VIII

Polyethylene terephthalate polymer chip is prepared by the method of Example III and poly(1,4-butylene terephthalate) polymer chip is prepared by the method of Example I. Fifty (50) parts of the poly(1,4-butylene terephthalate) polymer chip is then mixed with fifty (50) parts of the polyethylene terephthalate polymer chip, and the mixture is extruded through an annular pack under conditions as described in Example V except that the pack outlet temperature is maintained at 275° C.

The spun yarn with a birefringence range of 0.010 to 0.030 is drawn, heat set, and relaxed as previously described. The yarn is found to have a tenacity of 3.5 gpd, elongation of 44% and bending recovery of 65% when measured under the conditions previously described.

EXAMPLE IX

Melt blended polymers are prepared by the methods described in Example VIII, the specific blends having physical properties as set forth in Table II.

TABLE II

Polymer Composition	Tenacity, gpd	Elongation (%)	Bending Revocery, %
75% poly(1,4-butylene terephthalate) 25% polyethylene terephthalate	3.9	40	75
90% poly(1,4-butylene terephthalate) 10% polyethylene terephthalate	4.1	48	80

WHAT WE CLAIM IS:—

1. Crimped polyester filaments and staple fibre having a bending recovery of at least 65%, more than 6.0 crimps per crimped inch and more than 18% crimp and made from polyester whereof 50% or more by weight is a polymeric terephthalic acid ester of 1,4-butanediol or 1,3-propanediol.

2. Crimped polyester filaments according to Claim 1, consisting substantially wholly of the polymeric ester of 1,4-butanediol or 1,3-propanediol and having a bending recovery of at least 70%.

3. Crimped polyester filaments according to Claim 1, consisting of at least 75% of the polymeric ester of 1,4-butanediol and having a bending recovery of at least 75%.

4. Crimped polyester filaments according to Claim 1 and substantially as hereinbefore described.

5. Continuous filament yarns and tows and staple fibre made from any of the crimped filaments claimed in the preceding claims.

6. Carpets and other pile fabrics having a pile of continuous filament or staple fibre

yarns made from any of the crimped fila-
ments claimed in Claims 1 to 4.

7. Pillows and other resilient articles filled
with tows of staple fibre made from any of
5   the crimped filaments claimed in Claims 1
to 4.

8. Woven, knitted and non-woven fabrics

and batting made from any of the filaments
claimed in Claims 1 to 4.

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